

(19) JAPANESE PATENT OFFICE (JP)  
(12) PATENT JOURNAL (A)  
(11) JAPANESE KOKAI PATENT APPLICATION NO. 2001-288139

(43) Publication Date: October 16, 2001

(51) Int. Cl. <sup>7</sup>: C07C 51/265

51/487

63/26

// C07B 61/00

Identification Code: 300

Theme Code (Reference): 4H006

4H039

F Term (Reference): 4H006 AA02 AC46

4H039 CA65 CC30

No. of Claims: 5 (Total of 8 pages; OL)

Examination Request: Not requested

(21) Application No.: 2000-71476 (P2000-71476)

(22) Application Date: March 15, 2000

(31) Priority Claim No.: 2000-27626 (P2000-27626)

(32) Priority Date: February 4, 2000

(33) Priority Claim Country: Japan (JP)

(71) Applicant: 000005968

Mitsubishi Chemical Co., Ltd.

2-5-2 Marunouchi, Chiyoda-ku, Tokyo

(72) Inventor: Naoki Noguchi

Mitsubishi Chemical Co., Ltd.

Kurosaki Business Office

1-1 Shiroishi, Kurosaki, Nishi-ku, Yawata, Kyushu-shi, Fukuoka-ken

(72) Inventor: Takashi Komatani

Mitsubishi Chemical Co., Ltd.

2-5-2 Marunouchi, Chiyoda-ku, Tokyo

(74) Agent: 100103997

Akemori Hasegawa, Patent Attorney

[The amendments have been incorporated into the text of translation.]

## (54) METHOD FOR THE MANUFACTURE OF HIGH-PURITY TEREPHTHALIC ACID

### (57) Abstract

**Task:** To provide a method for producing high-purity terephthalic acid without deteriorating the product quality, in which the amount of virgin [defined later] water for use during the manufacture is reduced.

**Solving means:** Para-xylene is oxidized with molecular oxygen in a liquid reaction medium to obtain a mixture containing raw terephthalic acid, said mixture is subjected to additional oxidation with molecular oxygen without supplying para-xylene at a temperature higher than that in the reaction zone mentioned previously to manufacture a slurry containing terephthalic acid of a higher purity, the terephthalic acid is removed as a solid from said slurry, a solution is manufactured by the dissolution of the terephthalic acid solid mentioned previously in a liquid containing water, a hydrogenation treatment is carried out in the presence of a catalyst, and the solid-liquid separation of the reaction product obtained is conducted to manufacture high-quality terephthalic acid. Furthermore, at least a portion of the liquid obtained in said solid-liquid separation is supplied to the hydrogenation treatment.

## CLAIMS

1. A method for the manufacture of high-purity terephthalic acid having the following steps 1 through 5:
  - 1) para-xylene is oxidized with molecular oxygen in a liquid reaction medium to obtain a mixture containing raw terephthalic acid,
  - 2) said mixture is subjected to additional oxidation with molecular oxygen without supplying para-xylene at a temperature higher than that in the reaction zone mentioned previously in 1 to manufacture a slurry containing terephthalic acid of a purity higher than that of the terephthalic acid obtained in 1,
  - 3) the terephthalic acid is removed as a solid from said slurry,
  - 4) a solution is manufactured by the dissolution of the terephthalic acid solid mentioned previously in 3 in a liquid containing water, and a hydrogenation treatment is carried out in the presence of a catalyst, and
  - 5) the solid-liquid separation of the reaction product obtained in 4 mentioned previously is conducted to manufacture high-purity terephthalic acid.

2. A method for the manufacture of high-purity terephthalic acid, characterized by the fact that, in Claim 1, at least a portion of the liquid obtained in the solid-liquid separation of Step 5 is supplied to the hydrogenation treatment step in Step 4.

3. A method for the manufacture of high-purity terephthalic acid, characterized by the fact that, in Claim 1 or 2, the oxidation of para-xylene in Step 1 is conducted in a reaction zone at 140-210°C, and the additional oxidation in Step 2 is conducted in a reaction zone at 210-280°C.

4. A method for the manufacture of high-purity terephthalic acid, characterized by the fact that, in any of Claims 1 through 3, the transmittance of the terephthalic acid removed in Step 3 is more than 80%.

5. A method for the manufacture of high-purity terephthalic acid, characterized by the fact that, in any of Claims 1 through 4, the content of 4-carboxy benzaldehyde in terephthalic acid removed in Step 3 is less than 500 ppm by weight.

## DETAILED EXPLANATION OF THE INVENTION

[0001]

### TECHNOLOGICAL FIELD TO WHICH THE INVENTION BELONGS

The present invention relates to a method for the manufacture of high-purity terephthalic acid. In particular, it relates to a method for the manufacture of high-purity terephthalic acid, in which the treating load of effluent water is decreased by reducing the amount of impurities contained in the water purged from the reaction system, the amount of virgin water used and the amount of water discharged are reduced, and it is economically advantageous and environmentally excellent. Here, the "virgin water" is the water newly supplied to the manufacturing process during the manufacture of high-purity terephthalic acid. It refers to water that has not been used in the reaction in the hydrogenation treatment step of said manufacture. It is also possible that the water formed in the oxidation step is used as "virgin water".

[0002]

### CONVENTIONAL TECHNOLOGY

In general, high-purity terephthalic acid is manufactured by the purification of raw terephthalic acid obtained by the oxidation of para-xylene. As a method for the manufacture of raw terephthalic acid, it is common that para-xylene is oxidized with molecular oxygen in the

coexistence of a catalyst in a reaction medium. As an example of a common method for the manufacture of high-purity terephthalic acid by the purification of raw terephthalic acid, one can mention a method in which the raw terephthalic acid is made into a water slurry; after this is heated and dissolved, the hydrogenation purification is carried out to obtain terephthalic acid of a higher purity. In general, for the high-purity terephthalic acid, the judgment of product quality and the control are carried out by using the content of 4-carboxy benzaldehyde (to be called "4CBA" hereafter) as one of the intermediates in the oxidation reaction of para-xylene, the content of para-toluic acid (to be called "p-TA" hereafter) as a hydrogenated product of 4CBA, the transmittance of light at a wavelength of 340 nm (to be called "transmittance" hereafter) when the same product is dissolved in an alkaline aqueous solution, and so on as indices.

[0003]

In the process for the manufacture of high-purity terephthalic acid by the hydrogenation purification of said raw terephthalic acid, in general, many impurities formed in the oxidation reaction of para-xylene, in the hydrogenation reaction of raw terephthalic acid, and in other reactions are contained in the liquid separated from the solid high-purity terephthalic acid by solid-liquid separation after the hydrogenation reaction. As the impurities, 4CBA, p-TA, benzoic acid (to be called "BA" hereafter), and so on can be mentioned. Therefore, in general, water is discarded without recycling.

[0004]

In Japanese Kokai Patent Application No. Hei 5[1993]-58948, a method is proposed in which, during the manufacture of high-purity terephthalic acid, a liquid containing water is separated from the deposited terephthalic acid after the hydrogenation reaction, said liquid is recycled as such for use in the dissolution of raw terephthalic acid, and the amount of usage of virgin water is decreased. However, if the recycling of the liquid containing water is carried out by the method as proposed in said patent journal, it is inevitable that many impurities will accumulate in said liquid when the recycling ratio is high. As a result, the amount of said impurities contaminating the product is increased to a large extent. Because of this, the transmittance deteriorates and the quality of the high-purity terephthalic acid product is decreased.

[0005]

#### PROBLEMS TO BE SOLVED BY THE INVENTION

In the conventional methods like this, in the manufacture of high-purity terephthalic acid, the water-containing liquid separated from the deposited terephthalic acid after the purification

step contains many impurities and the load in effluent water treatment is increased. Furthermore, even if said liquid is recycled for use, the recycling ratio must be set at a low level in order to maintain the quality of the product. In the case of the industrial application of said method, the economic benefit is extremely slight. As a result of the accumulation of zealous investigations, the present inventors have achieved the following discoveries. In other words, between the step for carrying out oxidation by supplying para-xylene and a gas containing oxygen and the step for hydrogenation purification conducted after this, a step for conducting additional oxidation without supplying para-xylene at a temperature higher than the temperature for said oxidation step is introduced. By doing this, the content of impurities in the substance sent to the hydrogenation purification step is decreased very effectively. Furthermore, in regard to the water-containing liquid recovered from the solid-liquid separation carried out after said hydrogenation purification, by the introduction of the additional oxidation step mentioned previously, the content of impurities capable of causing a reduction in the quality of the product can be decreased very effectively. Moreover, while the amount of impurities capable of causing a reduction in quality is kept at an extremely low level as such, said liquid can be recycled for use in the hydrogenation purification step. The present invention provides a method for decreasing the amount of virgin water used during the manufacture of high-purity terephthalic acid, without deteriorating the quality of high-purity terephthalic acid as the product.

[0006]

#### MEANS TO SOLVE THE PROBLEMS

In other words, the gist of the present invention is a method for the manufacture of high-purity terephthalic acid having the following steps 1 through 5.

- 1) Para-xylene is oxidized with molecular oxygen in a liquid reaction medium to obtain a mixture containing raw terephthalic acid,
- 2) Said mixture is subjected to additional oxidation with molecular oxygen without supplying para-xylene at a temperature higher than that in the reaction zone mentioned previously in 1 to manufacture a slurry containing terephthalic acid of a purity higher than that of the terephthalic acid obtained in 1,
- 3) The terephthalic acid is removed as a solid from said slurry,
- 4) A solution is manufactured by the dissolution of the terephthalic acid solid mentioned previously in 3 in a liquid containing water, and a hydrogenation treatment is carried out in the presence of a catalyst, and
- 5) The solid-liquid separation of the reaction product obtained in 4 mentioned previously is conducted to manufacture high-purity terephthalic acid. Furthermore, the gist of the present invention is, more preferably, a method for the manufacture of high-purity

terephthalic acid characterized by the fact that at least a portion of the liquid obtained in the solid-liquid separation of Step 5 is supplied to the hydrogenation treatment step in Step 4.

[0007]

#### EMBODIMENTS FOR THE IMPLEMENTATION OF THE INVENTION

A detailed explanation in regard to the present invention is given in the following. First of all, in Step 1, para-xylene is oxidized with a gas containing molecular oxygen in a liquid reaction medium to obtain a raw terephthalic acid. At this time, it is desirable that generally more than 90 wt%, preferably more than 95wt %, of para-xylene is oxidized to terephthalic acid. As a liquid reaction medium during the implementation of said oxidation, in general, a lower aliphatic carboxylic acid can be used. In particular, acetic acid is preferred.

[0008]

A case using acetic acid as a solvent will be explained as an example in the following. The amount of usage of the acetic acid solvent is generally 2-6 times by weight with respect to para-xylene. Furthermore, it is also acceptable that a certain amount, for example, less than 10 wt%, of water is contained in said acetic acid solvent. As gases containing molecular oxygen, air, oxygen diluted with an inert gas, oxygen-enriched air, and so on can be used. However, from the equipment aspect, the cost aspect, and so on, in general, air is preferably used.

[0009]

In the oxidation of para-xylene, in general, a catalyst is used. The catalysts are generally materials containing cobalt, manganese, and bromine. As their specific examples, for cobalt compounds, cobalt acetate, cobalt naphthenate, cobalt bromide, and so on can be exemplified. For manganese compounds, manganese acetate, manganese naphthenate, manganese bromide, and so on can be exemplified. For bromide compounds, hydrogen bromide, sodium bromide, cobalt bromide, manganese bromide, tetrabromoethane, and so on can be exemplified. These compounds can also be used in combinations.

[0010]

In regard to the amount of usage of the catalyst, the amount of usage of the cobalt component calculated as cobalt metal with respect to acetic acid is 120-3,000 ppm by weight, preferably 200-2,000 ppm by weight. The amount of usage of the manganese component is 0.001-2 times, in an atomic ratio with respect to cobalt. Furthermore, if shown as the absolute amount of usage of the manganese component, it will generally be 1-300 ppm by weight,

preferably 5-280 ppm by weight, calculated as manganese metal with respect to acetic acid. The amount of usage of the bromine component is 0.1-5 times, preferably 0.2-2 times, in an atomic ratio with respect to cobalt. If the amount of usage of the catalyst is outside the ranges mentioned previously, the purity or the transmittance of the terephthalic acid obtained will be insufficient, acetic acid combustion will increase, and effectiveness is difficult to achieve. In particular, the amount of usage of the manganese component is important. If it is less than 0.001 times in an atomic ratio with respect to cobalt, there is a trend in which the reaction activity will decrease to a large extent. If it is more than 2 times, the precipitation of the manganese component will occur. This will contaminate the terephthalic acid. Disadvantages will easily occur, in which the quality of terephthalic acid as the product will deteriorate, the loss of acetic acid will increase, etc.

[0011]

It is desirable that the reaction temperature for the oxidation of para-xylene in Step 1 is generally 140-210°C, preferably 170-200°C, and especially preferably 175-198°C. If it is under 140°C, the reaction rate will decrease. If it is above 210°C, this will be undesirable since there is a trend in which the amount of loss of the acetic acid solution will increase due to its combustion. The reaction pressure is at least that at which the mixture is maintained in the liquid phase at the reaction temperature. In general, it is 0.2-5 MPa. The reaction is generally carried out in a continuous manner. Its reaction time (the average residence time) is 30-300 min. The water concentration in the reaction medium is generally 5-25 wt%, preferably 7-20 wt%. The adjustment of the water concentration can be conducted, in general, by removing the volatilized gas from the reaction vessel and purging, out of the system, a portion of the reflux liquid of the condensable components obtained by the condensation of said gas.

[0012]

The reactor for use in the present invention is generally a tank provided with a stirrer. However, the stirrer is not necessarily required. A gas bubble column type is also acceptable. A cooler is provided at the top of the reactor, and a supply inlet for a gas containing molecular oxygen is provided at the bottom. The gas containing molecular oxygen supplied from the bottom, after being utilized in the oxidation reaction, is withdrawn from the reactor as a gas component accompanying a large amount of the acetic acid vapor. After the removal of acetic acid by condensation in a reflux condenser, it is discharged as an oxidation effluent gas. The condensed liquid is partly purged from the system for the water content adjustment, and the remainder is recycled to the reactor.

[0013]

In the present invention, during the implementation of the oxidation reaction of para-xylene in Step 1, in a manner as described in Japanese Kokai Patent Application No. Hei 9 [1997]-278709, it is also acceptable that the oxidation effluent gas obtained by the condensation removal of condensable components from the gas withdrawn from the reactor is branched into two streams, with one being discharged out of the system and the other being continuously supplied into the reactor by circulation.

[0014]

In the present invention, after the oxidation reaction mentioned previously, additional oxidation can be carried out immediately at a temperature higher than said reaction temperature. If necessary, prior to this, another additional treatment can be carried out. As said additional treatment, for example, it is effective to carry out the additional oxidation (to be called "low-temperature additional oxidation") treatment of the reaction mixture of the previously mentioned oxidation reaction (the first reaction zone) in the second reaction zone maintained at a temperature lower than that in the first reaction zone, generally at 140-195°C. The reaction pressure is at least that at which the mixture is maintained in the liquid phase at the reaction temperature. In general, it is 0.2-5 MPa. The reaction is generally carried out in a continuous manner. Its reaction time (the average residence time) is 5-120 min. In the same manner as in the first reaction zone, as gases containing molecular oxygen to be supplied to said low-temperature additional oxidation, air, oxygen diluted with an inert gas, oxygen-enriched air, and so on can be used. However, from the equipment aspect, the cost aspect, and so on, in general, air is preferably used. Furthermore, its amount supplied is generally 1/5 to 1/10,000 or so of the amount supplied to the oxidation reaction in the first reaction zone. As a reactor for carrying out said low-temperature additional oxidation, any type can be used as long as it can be used in the first reaction zone.

[0015]

In the present invention, directly from the first reaction zone, or through the oxidation reaction in the second reaction zone, by the additional oxidation (to be called "high-temperature additional oxidation") in a reaction zone (the third reaction zone) at a temperature higher than that in the first reaction zone without supplying para-xylene, medium-purity terephthalic acid can be obtained. In the present invention, "medium purity" means a purity higher than that of the reaction product of the first reaction zone or that of a substance obtained by the further low-temperature additional oxidation of this, as well as a purity lower than that of the terephthalic acid obtained as a final product. For example, the medium purity refers to a quality level of a



4CBA content of less than 500 ppm and a transmittance of more than 80%. If raw terephthalic acid is manufactured by carrying out the oxidation reaction under ordinary conditions prior to the high-temperature additional oxidation, the 4CBA content is 800-5,000 ppm and the transmittance is less than 80%. If the medium-purity terephthalic acid is to be manufactured without the implementation of the high-temperature additional oxidation, in the oxidation reaction prior to this, it is necessary to increase the reaction temperature and/or the catalyst concentration. In this case, the amount of combustion of acetic acid is also increased, and the cost is higher in an unfavorable manner.

[0016]

The temperature of said third reaction zone is generally more than 200°C, preferably 210-280°C. The reaction pressure is at least that at which the mixture is maintained in the liquid phase at the reaction temperature. In general, it is 5-10 MPa. The reaction is generally carried out in a continuous manner. Its reaction time (the average residence time) is 5-120 min. In the same manner as in the first reaction zone, as gases containing molecular oxygen to be supplied to said high-temperature additional oxidation, air, oxygen diluted with an inert gas, oxygen-enriched air, and so on can be used. However, from the equipment aspect, the cost aspect, and so on, in general, air is preferably used. Furthermore, its amount supplied is generally 1/5 to 1/10,000 or so of the amount supplied to the oxidation reaction in the first reaction zone. The treating time is generally 5-120 min. As a reactor for carrying out said high-temperature additional oxidation, any type can be used as long as it can be used in the first reaction zone.

[0017]

Furthermore, said high-temperature additional oxidation can be carried out without further addition of the catalyst or with the addition of a small amount of the catalyst. In the case of the addition of the catalyst, in general, one with the same composition as that used in the first reaction zone can be used. However, it is also acceptable to change somewhat the composition of the catalyst to be added after the concentration inside the high-temperature additional oxidation reactor has been taken into consideration. Furthermore, the amount of the catalyst to be added is generally less than 10% of the amount of usage in the first reaction zone. By the crystallization treatment of the reaction mixture subjected to the high-temperature additional oxidation, a medium-purity terephthalic acid solid can be obtained. Said terephthalic acid is generally sent to the hydrogenation purification step after drying following the crystallization treatment. However, it is also acceptable to send this directly to the hydrogenation purification step, with the omission of said drying step.

[0018]

In the present invention, by increasing, to the medium purity level, the purity of the terephthalic acid to be sent to the hydrogenation purification step to be described later, the content of impurities contained in the water-containing liquid recovered after said purification step can also be decreased. As a result, even if said liquid is recycled for use in the hydrogenation purification step, it will be possible to control the amount of accumulation of impurities inside said step. It has been possible to increase the recycle ratio of said liquid while the quality of the product is maintained.

[0019]

As the hydrogenation purification step in continuation of this, a variety of methods can be used. For example, it is possible to mention a method in which the water-containing liquid is added into the previously mentioned raw terephthalic acid to make a slurry; this, in a state of being heated and dissolved, is subjected to a hydrogenation treatment in the presence of a hydrogenation catalyst, then crystallization and solid-liquid separation are carried out on the reaction product obtained to manufacture high-purity terephthalic acid. At this time, the raw terephthalic acid is generally supplied to the hydrogenation reaction system as a slurry of 20-35 wt% with respect to the water-containing liquid.

[0020]

As the hydrogenation catalysts, any catalyst publicly known to date can be used. For example, palladium, ruthenium, rhodium, osmium, iridium, platinum, iron, cobalt, nickel and so on supported on activated carbon can be mentioned. These catalysts can also be used in combinations.

[0021]

As reaction conditions for the hydrogenation purification reaction, it is common to carry this out at a reaction temperature of 255-300°C, a reaction pressure of 1-12 MPa, and a hydrogen partial pressure of 0.05-3 MPa. However, they are not restricted to these.

[0022]

It is common that the terephthalic acid purified by the hydrogenation reaction is removed as a solid by carrying out crystallization and solid-liquid separation. The crystallization conditions are selected by taking into consideration the yield of the solid deposited, the purity of the same solid, etc. In general, this is conducted at a temperature of 100-190°C and a pressure of 0.1-1.5 MPa. It is preferable that the crystallization is carried out in multiple stages. This is

carried out by a method such that the crystallization conditions in the final stage are 150-180°C and 0.3-1.4 MPa. At this time, the residence time in the crystallization tank is 5-200 min. In particular, if the temperature of the crystallization tank in the final stage is below the range mentioned previously, the amount of p-TA and other impurities deposited will increase drastically. Therefore, a disadvantage occurs in which the purity of terephthalic acid removed as a solid will decrease.

[0023]

In general, by carrying out solid-liquid separation after crystallization, terephthalic acid deposited in the crystallization step is separated from the liquid with water as the major component. The temperature and pressure conditions for the solid-liquid separation are 100-190°C and 0.1-1.5 MPa, preferably 150-180°C and 0.3-1.4 MPa. In general, in the case of having the crystallization step in multiple stages, as conditions for the crystallization tanks mention previously, conditions approximately equal to those of the final crystallization tank can be selected. As the apparatus for carrying out the solid-liquid separation, in general, a decanter centrifugal separator, a vacuum belt filter, a drum filter, or other apparatuses can be used. However, it is not to be restricted to these. Furthermore, it is also possible to use a combination of two or more of these apparatuses.

[0024]

The terephthalic acid obtained by the removal, via solid-liquid separation, of the solid deposited after the purification step is dried as such to yield a product. It is also acceptable that, after the implementation of washing by forming into a slurry with virgin water in a suspension-washing tank, the solid removed by the solid-liquid separation is dried to yield a product. The water used in said washing is removed as a liquid containing water by the solid-liquid separation. Since its content of impurities is sufficiently low, it can be recycled for use as such as the reaction medium during the hydrogenation purification of raw terephthalic acid.

[0025]

After the previously mentioned oxidation reaction step and the subsequent hydrogenation purification step, the liquid containing water separated from the deposited high-purity terephthalic acid by the solid-liquid separation, as such or after an additional treatment, is used in the dissolution of the medium-purity terephthalic acid mentioned previously, and is recycled to the hydrogenation purification step again. As the additional treatment, it is possible to mention, for example, a method in which impurities are further deposited by cooling said liquid, with the impurities being subjected to the solid-liquid separation. For example, said liquid is sent into a

tank in which the pressure is reduced to 9.3 kPa (70 torr) with a steam ejector or the like, and cooling to 40-50°C can be achieved by the condensation of the generated steam with a condenser. The liquid after the removal of the deposited impurities by the solid-liquid separation is recycled to the hydrogenation purification step again. For this separation, a centrifugal separator, a paffner [transliteration], a belt filter, a back filter, or the like can be used. However, it is not to be restricted to this.

[0026]

At this time, said liquid can be supplied by continuous circulation for use in the dissolution of terephthalic acid. It is also possible that, after being stored once in a separate location, this is withdrawn for use at a required amount corresponding to the demand. The amount of the recycle use is selected by taking into consideration the impurity concentration contained in said liquid, economies etc. It is 20-100 wt%, preferably 40-90 wt%, of the total amount of the liquid containing water separated, by the solid-liquid separation, from the terephthalic acid deposited after the purification step. Furthermore, in the selection of the amount of the recycle use, it is preferable to select an amount such that the impurities, such as the p-TA concentration, remaining in the high-purity terephthalic acid as the final product, are used as a yardstick, with the p-TA residual concentration being less than 200 ppm.

[0027]

Next, an embodiment of the present invention will be explained with reference to Figure 1. Figure 1 is a schematic diagram for the process of the present invention. First of all, a mixture (1) of a catalyst, a solvent, and para-xylene, along with a gas (2) containing molecular oxygen, are supplied into an oxidation reactor (3). The gaseous component withdrawn from said reactor (3), after the condensation removal of acetic acid and so on with a heat exchanger (4), is discharged as an oxidation effluent gas (5). Said condensed liquid, after a portion of it has been discharged out of the system as a purged portion (6) for water adjustment, is refluxed to the reactor (3). A substance (7) subjected to said oxidation treatment in the reactor (3) is transferred to a low-temperature additional oxidation tank (9) and subjected to an oxidation treatment with a small amount of a gas (8) containing molecular oxygen. A substance (10) subjected to said low-temperature oxidation treatment is heated beforehand with a heat exchanger (11) to a temperature higher than that in the reactor (3), then transferred into a high-temperature additional oxidation tank (13). It is subjected to an oxidation treatment with a small amount of a gas (12) containing molecular oxygen. A substance (14) subjected to said high-temperature additional oxidation treatment is crystallized in a crystallization tank (15). In Figure 1, the case of crystallization in two stages after the high-temperature additional oxidation treatment is shown.

However, the number of stages for crystallization is not to be restricted to this. One or more stages are acceptable. A substance (16) subjected to said crystallization treatment is separated by a solid-liquid separator (17) into a liquid component (18) and medium-purity terephthalic acid (19). Said medium-purity terephthalic acid (19) is made into slurry with a liquid (20) containing water in a mixing tank (21). Said slurry (22) together with hydrogen (23) is transferred into a hydrogenation purification reactor (24). A substance (25) subjected to said hydrogenation purification treatment is crystallized in a crystallization tank (26). In Figure 1, a case involving crystallization in one stage after the high-temperature additional oxidation treatment [sic] is shown. However, the number of stages for crystallization is not to be restricted to this. One or more stages is/are acceptable. A substance (27) subjected to said crystallization treatment is separated by a solid-liquid separator (28) into a liquid component (30) and a solid component (29). Said solid component (29) is dried with a dryer (31) to yield high-purity terephthalic acid (32). On the other hand, the liquid component (30) separated in the solid-liquid separator (28), if necessary, is partly discharged out of the system as a purged portion (33). The remainder is for recycle use. The recycled liquid (34), if necessary, is supplied and recycled into the mixing tank (21) as the liquid (20) containing water together with virgin water (35) supplied as make-up inside the system.

[0028]

#### APPLICATION EXAMPLES

The present invention will be further explained in detail with application examples in the following. However, the present invention is not to be restricted to the application examples as long as its gist is not exceeded.

#### APPLICATION EXAMPLE 1

By using a catalyst containing three components of Co, Mn, and Br as a catalyst, air as a gas containing molecular oxygen, as well as acetic acid as a solvent, medium-purity terephthalic acid was obtained according to the formulation to be described in the following. First of all, the oxidation reaction in the first reaction zone was carried out so that, inside the reactor, concentrations of Co, Mn, and Br were maintained at 270 ppm, 170 ppm, and 500 ppm, respectively, the temperature and pressure were 197°C and 1.68 MPa, respectively, and the residence time was 87 min. In continuation of this, the low-temperature additional oxidation treatment was carried out so that the temperature and pressure inside the reactor were 191°C and 1.42 MPa, respectively, and the residence time was 33 min. In continuation of this, the high-temperature additional oxidation treatment was carried out so that the temperature and pressure inside the reactor were 265°C and 5.49 MPa, respectively, and the residence time was 39 min.

As a result of analyses of the medium-purity terephthalic acid obtained by carrying out crystallization and solid-liquid separation in continuation of this, the 4CBA content was 248 ppm and the transmittance was 89.0%. This was purified by a series of continuous reactions maintained in the states to be described in detail in the following. The treated solid in a 30 wt% slurry form was transferred into said continuous reaction system. In said continuous reaction system, for the hydrogenation purification step, the temperature and pressure inside the reactor were 290°C and 8.73 MPa, respectively, and the residence time was 9 min. As a result of analyses of the terephthalic acid manufactured by the series of continuous reactions maintained in the states described previously, the 4CBA content was 1.7 ppm, the p-TA content was 15 ppm, and the transmittance was 97.3%. Good values were exhibited.

[0029]

#### APPLICATION EXAMPLE 2

The process up to the hydrogenation purification step was carried out in the same manner as in Application Example 1. Furthermore, the substance subjected to said treatment was crystallized. Out of the liquid component recovered from the solid-liquid separation, 50% was discharged from the system. The remaining 50% was recycled for use in making the previously mentioned medium-purity terephthalic acid into the slurry. At this time, the necessary amount of virgin water was supplied in order to make up the discharged portion of said liquid. As a result of analyses of the terephthalic acid manufactured by the series of purification steps maintained in the states described previously, the 4CBA content was 2.1 ppm, the p-TA content was 33 ppm, and the transmittance was 96.9%. Good values were exhibited. It is seen from this that, in the present application example, by the recycle use of 50% of the liquid containing water used in the hydrogenation purification reaction, the product quality was very slightly decreased.

[0030]

#### COMPARATIVE EXAMPLE

Terephthalic acid was manufactured by the same method as in Application Example 1 described previously except that the reaction temperature and the catalyst concentration in the oxidation reaction in the first reaction zone were increased and the high-temperature additional oxidation step was not carried out. The oxidation reaction in said first reaction zone was carried out so that, inside the reactor, concentrations of Co, Mn, and Br were maintained at 330 ppm, 215 ppm, and 660 ppm, respectively, the temperature and pressure were 202°C and 1.57 MPa, respectively, and the residence time was 62 min. In continuation of this, the low-temperature additional oxidation treatment was carried out so that the temperature and pressure inside the reactor were 189°C and 1.27 MPa, respectively, and the residence time was 34 min. These

conditions were virtually not different from the low-temperature additional oxidation treating conditions in Application Examples 1 and 2 described previously. In this comparative example, as a result of analyses of the medium-purity terephthalic acid prior to the implementation of the hydrogenation purification step, the 4CBA content was 1,865 ppm and the transmittance was 37.0%. As a result of analyses of the terephthalic acid product obtained by the implementation of hydrogenation purification, crystallization, and solid-liquid separation in the same manner as in Application Example 1, the 4CBA content was 6 ppm, the p-TA content was 87 ppm, and the transmittance was 94.4%. A low quality was exhibited. It is seen from this that, for example, in order to decrease the amount of impurities formed in the oxidation reaction in the first reaction zone, even though the reaction temperature and the catalyst concentration in said step are increased, the quality of the product is markedly decreased if no high-temperature additional oxidation treatment is carried out as in the application examples and the reference examples. In this comparative example, the medium-purity terephthalic acid was made into a slurry completely with virgin water without the recycle use of the liquid obtained by the crystallization and solid-liquid separation after the hydrogenation purification step. If the recycle of said liquid is further carried out, the quality of the product will deteriorate, of course.

[0031]

The various conditions for the experimental examples described previously are shown in Table I. The test results are shown in Table II.

[0032]

Table I

	Application Example 1	Application Example 2	Comparative Example	
Oxidation reaction (the first reaction zone)				
• Temperature	197	197	202	(°C)
• Pressure	1.68	1.68	1.57	(MPa)
• Residence time	87	87	62	(min)
• Catalyst composition (Co/Mn/Br)	270/170/500	270/170/500	330/215/660	(ppm)
Low-temperature additional oxidation				
• Temperature	191	191	189	(°C)
• Pressure	1.42	1.42	1.27	(MPa)
• Residence time	33	33	34	(min)
High-temperature additional oxidation				
• Temperature	265	265	-	(°C)
• Pressure	5.49	5.49	-	(MPa)
• Residence time	39	39	-	(min)

Hydrogenation purification				
• Temperature	290	290	290	(°C)
• Pressure	8.73	8.73	8.73	(MPa)
• Residence time	9	9	9	(min)
• Raw material concentration (*)	30	30	30	(wt%)
Recycle ratio (**)	0	50	0	(%)

[0033] -

(\*) The concentration of raw terephthalic acid or medium-purity terephthalic acid sent to the hydrogenation purification step

(\*\*) (Flow rate of the recycled liquid) / ((Flow rate of the recycled liquid) + (Flow rate of the purged liquid))

[0034]

Table II

	Application Example 1	Application Example 2	Comparative Example	
Prior to the hydrogenation treatment				
• 4CBA	248	209	1865	(ppm)
• Transmittance	89.0	84.7	37.0	(%)
Product				
• 4CBA	1.7	2.1	6	(ppm)
• p-TA	15	33	87	(ppm)
• Transmittance	97.3	96.9	94.4	(%)

[0035]

#### EFFECTS OF THE INVENTION

During the manufacture of high-purity terephthalic acid by the method of the present invention described previously, impurities contained in the water discharged from the reaction system can be decreased and the treating load for effluent water can be reduced. Furthermore, the amount of virgin water supplied in the hydrogenation purification of terephthalic acid and the amount of water purged can be reduced without causing the deterioration of the quality of the product. It is a manufacturing method that is economically advantageous and environmentally excellent. High-purity terephthalic acid can be manufactured.



[0036]

## BRIEF EXPLANATION OF THE FIGURE

**Figure 1** This is a schematic diagram of a process for the implementation of the present invention.

## EXPLANATION OF SYMBOLS

- 1: A mixture of a catalyst, a solvent, and para-xylene
- 2: A gas containing molecular oxygen
- 3: An oxidation reactor
- 4: A heat exchanger
- 5: An oxidation effluent gas
- 6: A condensed liquid purged portion
- 7: A substance subjected to the oxidation treatment
- 8: A gas containing molecular oxygen
- 9: A low-temperature additional oxidation reactor
- 10: A substance subjected to the low-temperature additional oxidation treatment
- 11: A heat exchanger
- 12: A gas containing molecular oxygen
- 13: A high-temperature additional oxidation reactor
- 14: A substance subjected to the high-temperature additional oxidation treatment
- 15: A crystallization tank
- 16: A substance subjected to the crystallization treatment
- 17: A solid-liquid separator
- 18: A liquid component separated by 17
- 19: A solid component separated by 17 (medium-purity terephthalic acid)
- 20: A liquid containing water
- 21: A mixing tank
- 22: Medium-purity terephthalic acid
- 23: Hydrogen
- 24: A hydrogenation purification reactor
- 25: A substance subjected to the hydrogenation purification treatment
- 26: A crystallization tank
- 27: A substance subjected to the crystallization treatment
- 28: A solid-liquid separator
- 29: A solid component separated by 28
- 30: A liquid component separated by 28

- 31: A dryer  
 32: Product high-purity terephthalic acid  
 33: A partly purged portion of the liquid component separated by 28  
 34: A recycled portion of the liquid component separated by 28  
 35: Virgin water

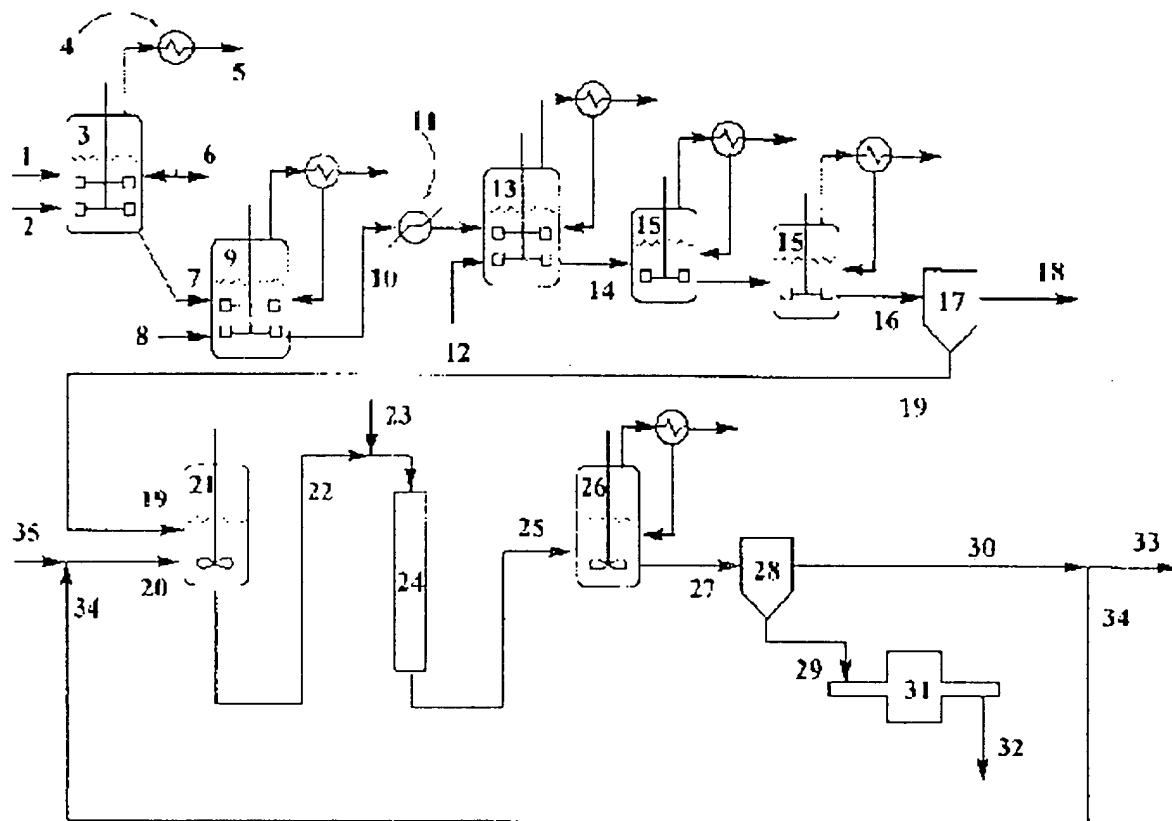


Figure 1

# PHOENIX

**TRANSLATIONS**

*...the height of Excellence...*

**Japanese Kokai Patent Application No. 2001-288139**

Translated from Japanese into English  
by Phoenix Translations Code No. 51-2890

2110-A White Horse Trail, Austin, TX 78757 Phone: (512) 343-8389,  
Toll-free: 877-452-1348, Fax: (512) 343-6721, Email: phoenixtranslations@ev1.net

Customer P.O. No.: 071702-16